LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although portions of this report are not reproducible, it is being made available in microfiche to facilitate the availability of those parts of the document which are legible.

3

LA-UR--89-1951

DE89 014258

TITLE THE LOS ALAMOS FOURIER-TRANSFORM SPECTROMETER: APPLICATIONS TO MOLECULAR SPECTROSCOPY

AUTHOR(S) Byron A. Palmer, Los Alamos National Laboratory
Robin S. McDowell, Los Alamos National Laboratory

SUBMITTED TO For presentation at the Seventh International Conference on Fourier Transform Spectroscopy - Fairfax, Virginia, June 19-23, 1989

To be published in Proc. SPIE - Int. Soc. Opt. Eng., v. 1145 (1989).

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

The Los Alamos Fourier-transform spectrometer: applications to molecular spectroscopy

Byron A. Palmer and Robin S. McDowell

University of California, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545

ABSTRACT

We outline design considerations and operating characteristics of the Los Alamos Fourier-transform spectrometer, a state-of-the-art instrument operating from 200 nm to 20 μm with a resolution of 0.0026 cm^{-1} and very high wave number and intensity accuracy. Recent work in molecular spectroscopy carried out with this instrument will be discussed, including N_2^+ spectra obtained in inductively-coupled plasmas; high-temperature spectra of diatomic molecules of astrophysical interest; high-resolution rovibrational fine structure; and Fourier-transform Raman spectroscopy of species in expansion-cooled gases.

1. INTRODUCTION

The Los Alamos Fourier-transform spectrometer[1] has been designed to operate from 200 nm in the ultraviolet to 20 μm and beyond in the mid-infrared, with a resolution of 0.0026 cm^{-1} (i.e., resolving powers of 10^7 to 10^5) and very high wave number and intensity accuracy. The instrument has been operational in the UV, visible, and near IR regions for over a year and recently has achieved full infrared operation. This paper will discuss the design and characteristics of the Los Alamos FTS, and some recent results in the recording and analysis of molecular spectra.

2. INSTRUMENT DESIGN

The Los Alamos instrument was designed along the same lines as the 1-meter rapid-scan FTS at the McMath Solar Telescope of Kitt Peak National Observatory.[2] The optical system is shown in Fig. 1. It is a two-arm folded-path Michelson interferometer with two moving 8-in (20-cm) cat's-eye reflectors, each with a parabolic primary and a secondary mirror at the focal point of the primary. The cat's-eyes are insensitive to minor tilts of the assembly, so there is no need for frequent dynamic alignment as is required with other interferometer mirror systems. To conserve space, the optical path is folded using two 8-in flat mirrors.

The beam splitter consists of two partially reflecting plates mounted one over the other, the top one dividing the incoming beam and the bottom one recombining the beams after reflection from the cat's-eyes. These plates are mounted in a rotating turret that holds three sets of beamsplitters and allows easy selection of the set appropriate to the wavelength region being studied. The optical arrangement provides a choice of two beam inputs, one (f/44) at the end of the instrument, and the other (f/22) at the side; two outputs to the detectors are located at the front.

The cat's-eye reflectors are moved on oil bearings by linear motors at constant speed. Each reflector carriage has one flat and two cylindrical bearings, which are supplied with oil pumped from a reservoir. The oil tubing and necessary electrical cables are flexible and are connected to the moving assemblies through swinger arms. Each mirror travels 1.15 m for a total optical path difference (retardation) of 2.3 m. There is provision for double-passing each interferometer arm to double this retardation, but this has not yet been implemented.

Fine motion control is provided by piezoelectric elements on the secondaries of the cat's-eye reflectors; these give servo frequency response up to 4 kHz, considerably reducing servo errors. The servo system employs a stabilized Zeeman-split He-Ne laser, whose output is divided by the beamsplitter, with one of the two orthogonally-polarized Zeeman components (separated in frequency by 1.6 MHz) selected by a polarizer in each arm. After traversing the interferometer section, these beams are recombined at the beamsplitter and the beat frequency is detected.

The servo system controls the mirror positions to within 3 Å, using three frequency synthesizers. One controls the laser Zeeman splitting, one controls the carriage position, and one provides pulses for the A/D converter to sample the interferogram. The Zeeman frequency is monitored by comparing the master frequency with the beat frequency of the laser at the laser head; the resulting error signal controls a solenoid that changes the magnetic field around the laser, and thus the Zeeman splitting. The beat frequency of the recombined beams is compared with the second control frequency; the error signal drives the linear motors and the piezoelectric elements in the cat's-eyes. To move the carriages, the control frequency is changed from the master frequency by the fringe rate, f_r.

This system has several advantages. Since the servo system error is updated at the Zeeman frequency and not the fringe rate frequency, full servo accuracy is achieved even when the mirrors are stationary. Fur-

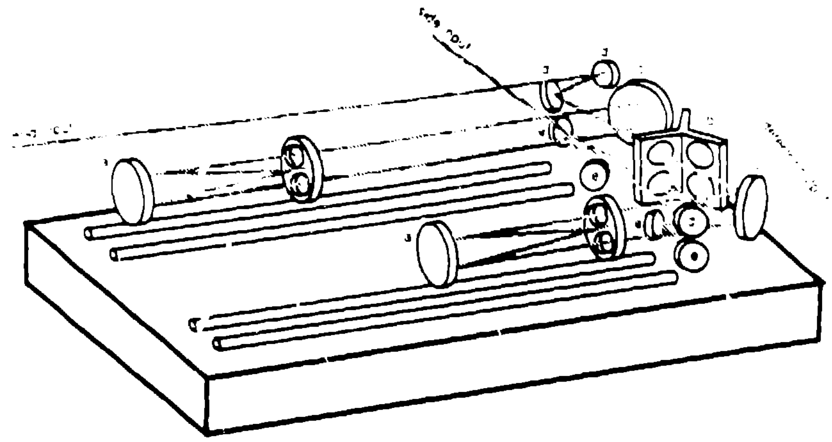

Figure 1. Optical system of the Los Alamos Fourier-transform spectrometer, showing the cat's-eye reflectors (a), beam splitter turret (b), folding mirrors (c), collimating optics (d), and detector optics (e).

ther, the mirrors can be moved at any speed that the frequency synthesizers can provide, from the minimum of 1 mHz to the maximum of 2 MHz less the Zeeman frequency (1.6 MHz), or 400 kHz. An important advantage for visible FTS work is the ability to select almost any free spectral range (FSR), because the FSR is determined by the fringe rate f_r and the sampling rate f_s, where f_s is derived from the third frequency synthesizer. The free spectral range is

$$FSR = \sigma_r f_s / 2 f_r ,$$

where σ_r is the laser wave number. The maximum sample rate is determined by the maximum rate at which the data can be coadded and stored to disk, presently 5 kHz.

The digitizing electronics have an effective 22-bit dynamic range (4×10^6), provided by seven 16-bit A/D converters and seven range amplifiers, each differing by a factor of two. Each interferogram point has a 16-bit mantissa and a 3-bit exponent. Since the individual converters and range amplifiers can never be perfectly matched, we use an 18-bit D/A converter to calibrate the A/D converters, allowing us to correct the converted data for differing offsets in each converter and for the differing gain in each converter/amplifier. A digital filter in the system eliminates noise from frequencies outside the region of interest, ensuring full 22-bit accuracy.

The instrument is mounted on an optical table that is supported by air bags and automatic leveling devices. The entire assembly is contained in a 14×7-ft cylindrical vacuum tank. All important optical elements can be adjusted externally.

The FTS is housed in a specially designed 3400-sq.ft. building that contains, in addition to the main spectrometer laboratory, smaller rooms for setting up experiments, a computer room, and offices. Adjoining the spectrometer room is a radiation laboratory with a glove-box train having an optical port with access to the instrument, enabling radioactive light sources to be studied without danger of contamination. Provision has been made for a roof-mounted heliostat for solar and atmospheric spectroscopy.

3. DATA REDUCTION

The servo computer acquires and coadds the data from the A/D converter system. We normally record double-sided interferograms for better signal-to-noise ratios and to eliminate potential phase problems. At the end of each run, the interferogram is transferred to a Macintosh computer for processing, using the Cooley-Tukey fast Fourier transform (FFT) algorithm. A 1-million-point transform in double precision now requires 21 minutes; a full 4-million-point transform (the present limit, determined by disk storage) takes 1 hour 34 minutes.

The spectra can then be analyzed using programs developed at Los Alamos for Macintosh computers. Capabilities include spectrum plotting, line file generation using several different line-finding methods (including fitting the line profile to a Voigt function), and interactive line file editing with simultaneous display of the spectrum and the file of line frequencies. Special options include spectrum subtraction; intensity correction using an intensity calibration curve determined from a scan of a standard light source; and exporting spectrum files in formats compatible with other computers.

4. INSTRUMENT SPECIFICATIONS AND STATUS

The design goals and present status of the Los Alamos FTS are summarized in Table 1. The instrument has met or is very close to meeting almost all of its design specifications. A few of these deserve special comment:

The lower spectral range given in Table 1 is the shortest wavelength observed to date, that of a Ca line in a hollow-cathode discharge. The longest wavelength was observed while examining filters in the IR detectors with a Globar source, but spectral absorption lines have also been recorded at nearly these wavelengths (CO_2 at 15 μm)

Spectral resolution is of course determined by the maximum optical retardation and all tests have indicated that the instrument performs as expected in this regard. Figure 2 shows a resolution test on a portion of

Table 1. Los Alamos FTS Status and Design Goals

Specification	Current	Design Goal
Spectral coverage	0.21 - 18.5 μm	0.20 - 20+ μm
Resolution, single pass	0.0026 cm^{-1}	0.0026 cm^{-1}
Resolution, double pass	NA	0.0013 cm^{-1}
Sample rate f_s	5 kHz	5 kHz
Data fringe rate f_f	10 kHz	10 kHz
Servo error	1-5 mfringe	1 mfringe
Maximum transform size	4 M	4 M
A/D amplifier noise level	20 μV	20 μV
S/N ratio	$10^3 - 10^5$	10[illegible] - 10^6
Wave number accuracy	~0.0005 cm^{-1}	0.0001 cm^{-1}
Intensity accuracy	?	0.1 %

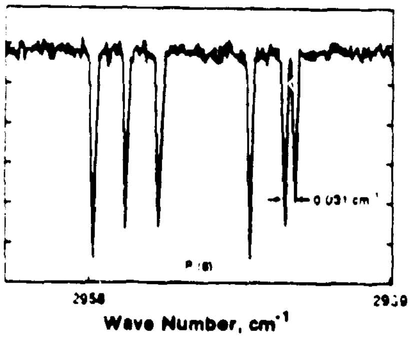

Figure 2. The P(6) manifold of the ν_3 stretching fundamental of CH_4. Sample pressure 1 Torr.

the methane fundamental originating at 3019 cm^{-1}. The resolution calculated for this run was 0.0054 cm^{-1}. The only line-broadening mechanism effective at this low pressure is that due to the Doppler effect, calculated to be 0.0092 cm^{-1}. Taking the root-sum-square of the instrumental and Doppler widths yields an expected fwhm of 0.0107 cm^{-1}, which compares satisfactorily with measured linewidths of 0.011 ± 0.001 cm^{-1} in Fig. 2.

The servo error increases with f_f because of the linear motors, which are two-phase and have dips in the power levels corresponding to the magnet period. For visible and UV work, f_f is small enough that the servo error is less than 1 millifringe. In the infrared, f_f increases, as does the servo error, but the resulting error in the interferogram actually decreases. We therefore have no plans to try to improve the servo error. The sample rate f_s is determined by the coadding and disk access times and could be improved with faster disks and/or faster processors.

The wave number accuracy was estimated by comparing the visible spectrum of a uranium hollow-cathode lamp between 20,000 and 26,000 cm^{-1} (385 - 500 nm) with line positions in the standard uranium atlas.[3] The estimated accuracy of the atlas data is 0.001 cm^{-1} as determined by wavemeter measurements and by energy-level fitting from the observed wave numbers. Measurement of some 200 lines resulted in a standard deviation of fit between atlas and FTS data of 0.00067 cm^{-1}. Considering the line-finding methods used and the signal-to-noise levels in the two data sets, this is approaching the theoretical limit for the accuracy. Further measurements of line frequencies will be made in the infrared, where standards of higher precision are available.

We have yet to check carefully the intensity accuracy, especially the zero line in absorption spectra. We hope to approach this problem in coming months.

Table 2 lists the beamsplitters and detectors that are currently in use.

We will now discuss some results in molecular spectroscopy that have been obtained over the past year using the Los Alamos FTS.

5. N_2^+ VIOLET TRANSITIONS

Helium inductively coupled plasmas are useful for the sensitive detection of elements, especially those with relatively high ionization potentials. Diatomic nitrogen (as N_2 or N_2^+) is a convenient temperature indicator in such plasmas.[4] The first negative band of N_2^+ has several advantages for such use: the (0,0) bandhead at 391 nm is in an easily accessible spectral region; the Q branch is very weak, reducing the line density relative to that in the N_2 second positive series (which is also used as a temperature probe); and the rotational structure can be adequately resolved at moderate resolution (<0.25 cm^{-1}).

This work employed a He-ICP torch designed for high efficiency at low flow rates and described in detail elsewhere.[5] With nitrogen in the flow, the only strong emission from 250 to 1150 nm is in four bands, all in the near ultraviolet and due to molecular nitrogen:

Table 2. Beamsplitter and Detector Ranges

Spectral region	Beamsplitters	Detectors
UV - VIS (200-800 nm)	Ag-coated Suprasil	1P28A photomultiplier tube
Near IR (0.8-2.5 μm)	Ge-coated CaF_2	InSb
Mid IR (1.5-20 μm)	Ge-coated KCl	InSb; Ga-doped Si

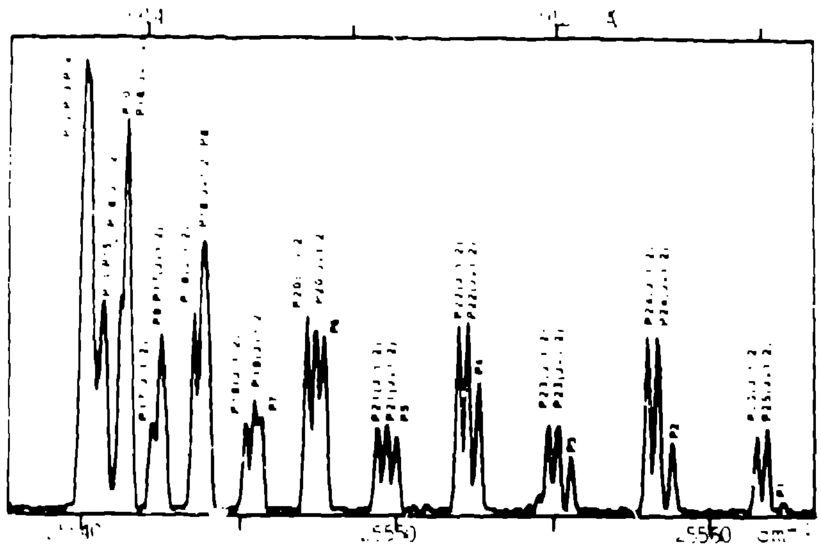

Figure 3. The P branch of the N_2^+ first negative group.

N_2^+ 1NG: $B^2\Sigma_u^+-X^2\Sigma_g^+$ (0-0) (Head at 3914 Å)
N_2^+ 2PG: $C^3\Pi_u-B^3\Pi_g$ (0-2) (3804 Å)
(0-1) (3577 Å)
(0-0) (3371 Å).

Twenty scans of these bands were made in 1 hr 17 min, each with 889,219 points, zero-filled to 2^{20} (1,048,576) points for transformation. The resolution, 0.09 cm^{-1}, is sub-Doppler for N_2 at plasma temperatures. The spectra are unapodized.

The first negative bands of N_2^+ were chosen for analysis. These are well known from laboratory and astronomical spectra (especially in twilight emission, auroras, and comet tails).[5] Dick et al.[6] photographed these bands on 5-m and 9.15-m vacuum grating spectrographs using a hollow cathode source, and reported frequencies with a precision of 0.01 cm^{-1}. These results were analyzed by Gottscho et al.,[7] who considered the effects of the perturbation between the $B^2\Sigma^+$ and $A^2\Pi_u$ states (the $C^2\Sigma_u^+$ state did not have to be considered).

The P branch of the N_2^+ 1NG is shown in Fig. 3. The band origin is off the illustration to the right; P-branch lines beginning with P(1) extend to lower frequencies, form a bandhead at P(12-14), 25539.9 cm^{-1}, and reverse direction. For P(16) and higher the doublet splitting is apparent. The alternation of line intensity (even:odd = 2:1) due to the nuclear spin statistics is unmistakable in both branches. Since the ratio of intensities in the P:Q:R branches is, to a first approximation,[3] $(J+1):(2J)^{-1}:J$, the Q branch is not evident.

The analysis of this band is summarized in Table 3. We used a least-squares fit of combination differences for the doublet-split transitions K = 18 to 36 to determine the rotational constants B and the centrifugal distortion constants D in the upper (') and lower (") states, and for the difference between the spin-rotation coupling constants γ for the two states. The band origin $\tilde{\nu}_0$ was found from a polynomial fit of the unresolved transitions K = 0 to 7.

Table 3 shows the results using our measured frequencies; the constants from a similar analysis of the frequencies of Dick et al.[6]; and the final constants given by Gottscho et al.[7] from their deperturbation analysis. The latter treatment yields a number of additional constants: perturbing terms in

Table 3. Results of Fitting N_2^+ 1NG: $B^2\Sigma_u^+-X^2\Sigma_g^+$ (0,0) (cm^{-1})

	LANL (1989)	Similar fit of data of Dick et al. (1978)	Gottscho et al.: deperturbation fit of Dick's data (1979)
Polynomial fit (K = 0-7):			(K = 0-56):
$\tilde{\nu}_0$	25566.017(2)	25566.061(1)	25566.05(2)
Combination differences (K = 18-36):			
B'	2.07513(8)	2.07482(8)	2.07433(4)
B"	1.92237(1)	1.92198(5)	1.92205(4)
$D' \cdot 10^6$	6.78(5)	6.74(5)	6.28(3)
$D" \cdot 10^6$	5.94(1)	5.86(3)	5.90(3)
$\gamma' - \gamma"$	0.0163(2)	0.0163(2)	0.0148
			(+ perturbing & higher-order terms)

the Hamiltonian matrix elements connecting the A and B states; and, because it included transitions with higher angular momentum quantum numbers, terms of higher order in J or K.

Several interesting conclusions can be drawn from Table 3. We note that the deperturbation does not improve the uncertainties in the ground-state constants B" and D" over the results obtained from combination differences with the perturbation neglected. This is expected because the A-B interaction does not affect the ground state X. The uncertainties in B" and D" thus reflect the experimental scatter in the measured frequencies. The uncertainties in these constants using the Los Alamos FTS data are significantly less, and suggest that ours is a better data set, at least in terms of relative frequency measurements. On the other hand, the excited (B) state constants B' and D' are improved by the deperturbation, as one would expect, and the uncertainties in these constants as obtained from our data would presumably decrease significantly with such a treatment.

The band origin ν_0 obtained from our data differs by 0.044 cm^{-1} from that given by the grating frequencies. This reflects a consistent calibration difference of that amount between the two data sets. Dick et al.[3] took great care with their calibration, superimposing standard lines from an iron hollow cathode on their plates. Our frequencies were obtained using a derivative approach to line finding that should be accurate to 1/100 of the line width, or better than 0.001 cm^{-1} for these lines. But the absolute frequencies were uncalibrated: we did not include any standard lines to correct for alignment effects on the frequencies. In any case, it is worth noting that our frequencies obtained by direct readout from the computer program, but without any special attention to calibration, agree with a carefully calibrated data set of the same band to within one part in 580,000, and the statistics of the fit suggest that the scatter in our frequencies is significantly less than that in the earlier data.

We intend to carry out a full deperturbation fit of these data, but after we have considered the calibration problem further. We will also consider in more detail the relative intensities of these transitions, their consistency with theoretical predictions, and their use in determining the rotational temperature in plasmas.

6. FT-RAMAN OF FLOW-COOLED GASES

As part of a program to study loosely-bound molecular complexes, Steven J. Buelow and David M. Harradine of Los Alamos have used the FTS to record Fourier-transform Raman spectra of gases cooled by supersonic adiabatic expansion through a nozzle. Spectra of the Q branch of the vibrational fundamental of N_2 are shown in Fig. 4. At a resolution of 0.04 cm^{-1} all but the lowest J values are resolved, and the 2:1 intensity alternation due to nuclear spin statistics is obvious. In the jet expansion spectrum the population has collapsed down to the lowest few angular momentum states. A fit of the Boltzmann factor to the line intensities indicates a rotational temperature of about 40 K in the expanding gas.

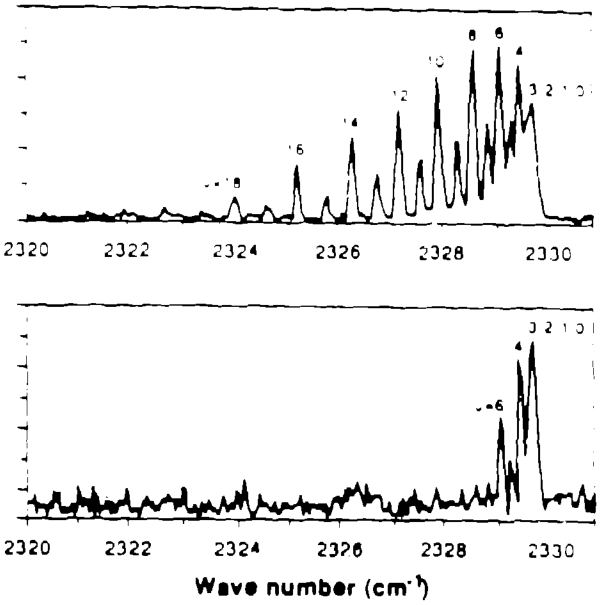

Figure 4. Demonstration of FT Raman spectroscopy of expansion-cooled gas. The N_2 Q branch at 2330 cm^{-1} as recorded with Ar^+ excitation at 488 nm; resolution ca. 0.04 cm^{-1}. The upper panel shows Raman scattering from 475 Torr N_2 in a static cell at 290 K; the lower panel, that from N_2 in a jet expansion at ca. 40 K. Collection time was 2 hr for both spectra.

7. EMISSION SPECTRA OF DIATOMIC SULFIDES

Sumner P. Davis and Mark C. Abrams (University of California, Berkeley) and Raymond J. Winkel Jr. (United States Military Academy) have used the FTS to observe emission spectra of diatomic sulfides. Such molecules as CaS, YS, LaS, and CeS are of astrophysical interest because they may contribute to the spectra of some cool (S-type) stars.

In a typical experiment, LaS powder was heated in a King-type carbon furnace to a temperature of 2200°C. Emission from LaS in the vapor above the powder was focused into the entrance aperture of the FTS, and the spectrum recorded from 625 nm to 1.25 μm. The spectrum clearly showed five four-headed bands between 700 and 850 nm, first identified by Marcano and Barrow in 1970.[4] In addition, another series of more intense bands, each having four heads degraded to the red, was found at longer wavelengths. A portion of the 0-1 bandhead near 1 μm is shown in Fig. 5.

The vibrational transitions have been identified, as shown in Table 4, which lists the leading head in each band. The 0-0 band-

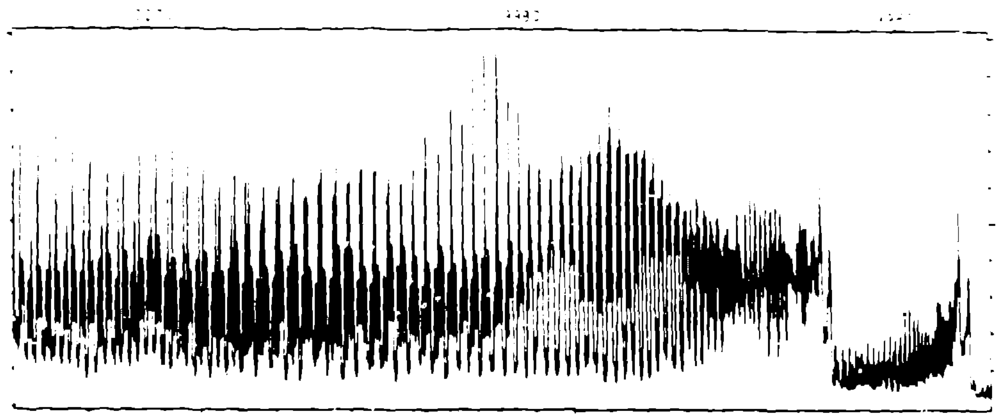

Figure 5. A portion of the 0-1 band of LaS at 2200°C. Resolution was 0.016 cm^{-1}, with eight 8-minute scans coadded. The scale at the top of the figure is in Å, that at the bottom in cm^{-1}.

Table 4. Vibrational Assignments in LaS

v'-v"	ν, cm^{-1}
0-3	9134
0-2	9587
0-1	10041
1-1	10452
1-0	10906
2-0	11316
4-1	11676

head, expected at 10,495 cm^{-1}, was not observed. Rotational analysis of these transitions is in progress.

8. CONCLUSIONS

The Los Alamos Fourier-transform spectrometer has demonstrated its effectiveness at recording high-resolution data of excellent quality throughout the ultraviolet, visible, and near infrared regions. We anticipate a great increase in the number of molecular spectroscopy problems attacked with this instrument as its region of routine operation is extended into the mid-infrared.

9. ACKNOWLEDGMENT

This work wa supported by the United States Department of Energy, and by Los Alamos National Laboratory's Chemical and Laser Sciences Division. We thank the various individuals cited in the text for permitting illustration and discussion of data obtained for them. Invaluable help in constructing the instrument has been provided by Douglas E. Hof.

10. REFERENCES

1. B. A. Palmer, "The Los Alamos Fourier Transform Spectrometer," Los Alamos National Laboratory Report LALP-85-16 (Aug. 1985).

2. J. W. Brault, J. Opt. Soc. Am. 66, 1081 (1976).

3. B. A. Palmer, R. A. Keller, and R. Engleman Jr., "An Atlas of Uranium Emission Intensities in a Hollow Cathode Discharge," Los Alamos Scientific Laboratory Report LA-8251-MS (July 1980).

4. T. J. Manning, B. A. Palmer, and D. E. Hof, Anal. Chem. 61, 1052 (1989).

5. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd ed. (Van Nostrand Reinhold, New York, 1950).

6. K. A. Dick, W. Benesch, H. M. Crosswhite, S. G. Tilford, R. A. Gottscho. and R. W. Field, J. Mol. Spectrosc. 69, 95 (1978).

7. R. A. Gottscho, R. W. Field, K. A. Dick, and W. Benesch, J. Mol. Spectrosc. 74, 435 (1979).

8. M. Marcano and R. F. Barrow, J. Phys. B3, L121 (1970).